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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

THE SIGNIFICANCE OF CHANGING ATOMIC VOLUME.

IV.—THE EFFECTS OF CHEMICAL AND COHESIVE INTERNAL
PRESSURE.

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IN the previous papers* upon this subject, it has been shown that there are many facts pointing toward the existence of a causal relationship between the volume occupied by solids and liquids and their internal pressures of cohesion and chemical affinity.

If a relation between the volume and internal pressures really exists, the volume occupied by the gram-equivalent of a solid becomes as important and essential a property of material as any other property.

In attempting to explain the facts with the help of the atomic hypothesis, there are two possible alternatives, — either a relatively incompressible atom exists within a compressible space, or else the atom itself is compressible, and in a solid or a liquid comes into contact with its neighbors. The former hypothesis is the one usually accepted; but it seems to me to be hampered by several insuperable difficulties. The nature of the supposed empty space between the molecules of a solid is not easy to imagine; for if it is due to the impact of the thermal vibrations of a small, hard particle, the difference between a solid and a gas is not sufficiently explained. Moreover, even at the lowest attainable temperatures, where the thermal vibration must be scarcely perceptible, ice occupies only about half the volume of the solid oxygen and hydrogen from which it may be made.† Such a large change in volume seems incredible, if it is

* Richards, These Proceedings, **37**; 1 (1901), 399 (1902); **38**, 293 (1902); also *Zeitschr. phys. Chem.*, **40**, 169, 597 (1902); **42**, 129 (1902).

† Dr. Frederick Soddy has kindly called my attention to this circumstance, the facts having been reported by Professor Dewar in an Address at the British Association, 1903.

imagined to be due to a restriction of thermal vibrations already almost infinitesimal.

These facts add strong support to the many-sided inference drawn from other facts that some repulsive tendency other than heat-vibration must be the cause of the permanent volume of solids and liquids — some tendency which is an intrinsic property of the atoms themselves. If so, this property must exist in the atoms of a gas as well as in those of a solid and liquid, and must also in a gas prevent the actual collision of the atomic centres, and thus take part in the “covolume” of the equation of van der Waals. This conclusion is not in any way inconsistent with the kinetic theory of gases, — in a gas the compressible molecules must still be supposed to be separate and to produce pressure by the momentum of their impact. In this connection it might be well to call attention to other evidence to be drawn from the viscosity of gases, that the bulk of polyatomic gas-molecules must be of the same order as that of monatomic gas-molecules. Noyes and Goodwin* found that the viscosity of mercury vapor seems to show its molecule to be about the same bulk as the molecule of carbon dioxide, and they sum up their investigation with these words: “These results indicate that the *atoms and molecules are of the same order of magnitude*, and that the spaces between the atoms within the molecule, if any exist, are not large in comparison with those occupied by the atoms themselves.”

In short, the “atomic environment” is really the volume which comes into consideration in all cases where the atomic volume is to be considered at all, and hence should be considered as the true volume of the atom. The conception of a hard, central particle is unnecessary, and assumptions concerning the supposed volume of the atomic centre must be of the most vague and hypothetical character, since this supposed volume never comes within the range of direct relative measurement. Since the measurable atomic volume is compressible, it is reasonable to assume that the atom is compressible, and that this atomic elasticity affords the possibility of heat vibration in solids and liquids composed of contiguous particles.

Some of the many other arguments in favor of this point of view have been already recounted in the three previous papers, and need not be recapitulated here. The object of the present paper is to bring a greater degree of numerical accuracy into the interpretation of the facts, and to

* A. A. Noyes and Goodwin, These Proceedings, **32**, 235 (1897). Professor Noyes has kindly called my attention to this work. See also Lord Rayleigh, Phil. Trans., 186 A, 187 (1895). Schultze Drude's Ann. (4) **5**, 140 (1901).

show that the more closely the data are scrutinized, the more emphatic is their support of the somewhat revolutionary hypothesis of atomic compressibility. The fact that this should be the case is in itself a strong support of the hypothesis; for fallacious arguments lose weight on closer scrutiny instead of gaining weight.

As has been already pointed out, the chief omission in all other work on the subject of changing atomic volume * has been the lack of attention to the compressibilities of the substances concerned. If the pressure of affinity causes a compression of the atomic volume, it is clear that a given affinity will produce a greater change of volume when the atomic volume is easily compressible than when it is only slightly compressible. This matter will be considered at greater length in this paper than has ever been possible before, since a number of appropriate compressibilities have just been determined in this laboratory for the first time, as well as several especially important specific gravities.

Another question, which must also receive consideration, is the varying intensity and nature of the affinities causing combination and cohesion. Do *both* of the two affinities, the chemical and cohesive, which together determine the stability of solids and liquids, exert internal pressure; and what effect does each of these have upon the volumes of substance?

These questions are so closely related that they may best be discussed in a single thesis. Indeed, owing to the complexity of the subject and the scarcity of exact data, the verdict of each answer is needed to sustain that of the other.

In the first place, the question of compressibility may be taken up.

* It is a pleasure to call attention here to the entirely independent work of J. Traube in this direction. By an interesting coincidence he published in Drude's *Annalen*, **5**, 550 (June 20, 1901), the following statement: "Das Atomvolumen eines Elementes ändert sich vielmehr von Stoff zu Stoff; es ist um so kleiner, je grösser die Anziehung zu den benachbarten Atomen ist," while on June 15 of the same year there appeared in the *Proceedings of the American Academy*, **37**, 17, my version of the same relationship: "*The atomic volume is not constant, but a function of pressure and temperature and probably of electric stress.*" By pressure was meant the internal pressure caused by affinity. In his pamphlet, "Über den Raum der Atome" [Ahrens's Sammlung. chem. und chem.-techn. Vorträge IV. 256 (Stuttgart, 1899)] Traube anticipated several points contained in his paper of 1901, and in my work in the same year, but this pamphlet was wholly unknown to me at the time. The fabric of Traube's reasoning is complicated by his hypothetical assumptions of "Covolumen" and "Kernvolumen," "gebundener" and "freier Aether;" but nevertheless he deserves the credit of having appreciated the importance of many of the facts. The question of priority is of little consequence, especially since Müller-Erbach (1881) had priority over both.

The effect of varying compressibility is best studied in series of elements possessing large compressibilities, for in these cases the variations are more evident. Hence there were determined for this purpose the compressibilities of chlorine, bromine, and iodine by Richards and Stull, and of lithium, sodium, and potassium by Richards and Bonnet.*

The values thus found, expressed in fractional decrease in volume for an increase of pressure of a kilogram per square centimeter, are given below :—

		Specific Gravity at 20°.	Atomic Volume.
Chlorine	[0.00011]	1.412	25.0
Bromine	0.000061	3.121	25.6
Iodine	0.000013	4.940	25.7
Lithium	0.000011	0.552 †	12.7
Sodium	0.000018	0.972 †	23.7
Potassium	0.000032	0.870 †	45.0

The value for chlorine is only an approximation, being computed from that of chloroform, carbon tetrachloride, and other analogous compounds, but it is sufficiently exact for the present purpose. These values justify the previous choice of chlorides, bromides, and salts of potassium in order to show in as marked a fashion as possible the effects of affinity in causing volume change, since the three elements, chlorine, bromine, and potassium, are unusually compressible. In a previous paper ‡ the choice of these three elements was made on the basis of their large coefficients of thermal expansion, for this property is more or less closely associated with compressibility, as the rule of Dupre § indicates.

A cursory study of the above table of compressibilities leads one immediately to predict that, with a given affinity, a greater change in volume would be caused in the formation of a salt of potassium than

* Of these investigations the first has already been printed in Publication No. 7 of the Carnegie Institution of Washington, and the second will soon appear in the same series.

† The specific gravities of these three alkali-metals were determined by Richards and Bonnet, and will soon be published.

‡ Richards, These Proceedings, **37**, 399 (1902).

§ See, for example, Ostwald, Lehrbuch, **1**, 394 (1891).

in one of sodium, and a greater change in one of sodium than in one of lithium. If we use heats of formation as indices of the free-energy change, or the work which may be done by affinities (a proceeding which is permissible in the case of these simple binary salts because of the small change of heat-capacity which occurs when they are formed from the elements*), we find that this prediction is fully

	Specific Gravity of Salt.	Sum of Atomic Volumes of Elements.	Molecular Volume of Salt.	Contraction, C.	Heat of Formation, H.	Quotient, $\frac{C}{H} \times 100$.
LiCl	2.07 †	37.7	20.9	16.8	383 ‡	4.3
NaCl	2.14	48.7	27.2	21.5	399	5.4
KCl	1.94	70.0	37.8	32.2	427	7.6
LiBr	3.46 †	38.2	25.2	13.0	334	3.9
NaBr	3.08	49.2	34.2	15.0	359	4.2
KBr	2.72	70.5	44.2	26.3	398	6.6
LiI	4.05 †	38.4	33.1	5.3	257	2.1
NaI	3.65	49.4	41.4	8.0	289	2.8
KI	3.07	70.7	53.8	16.9	335	5.1

* Richards, These Proceedings, **38**, 293 (1902). In the last paper upon this subject, it should have been made clear that the statement concerning the possible application of the heat-capacity relation to electrolytic dissociation is applied to very dilute solutions only by extrapolation, since no data exist for the heat-capacities of solutions more dilute than half normal. Professor Nernst has kindly pointed out to me that in case this relation really holds in very dilute solutions the coefficients obtained by him and by Jahn would acquire a special significance, their application to the facts remaining unchanged. This circumstance has nothing to do with the cases considered in the present paper; it is alluded to now only because I regret that in the previous discussion a possible inconsistency was suggested, which does not really exist.

† These results are due to careful experiments very kindly made in this laboratory by Dr. G. P. Baxter. The results of F. W. Clarke are undoubtedly too low, since the salts are hard to prepare pure. The value of the specific gravity of lithium, 0.552, is due to experiments made here by Richards and Bonnet.

‡ Because the heats of formation of chlorides as given in the text-books always refer to gaseous chlorine, there must be subtracted from them the latent heat of evaporation of liquid chlorine. The molecular latent heat of evaporation of chlo-

borne out by the facts concerning either chlorides, bromides, or iodides of these three metals. In every case the value of the fraction

$$\frac{\text{change of volume}}{\text{heat of formation}}$$

grows smaller as the compressibility of the metal is less. In other words, a given energetic effect is shown to produce a smaller change of volume whenever the compressibility is smaller. The facts are given in the tables below. The first table compares the different metals combined with a given halogen.

As has been said, the prediction is fully verified. The quotient of the contraction divided by the heat of formation is always smaller when the compressibility is smaller. Exactly the same phenomenon is to be observed if the several halogens be varied, in combination with a given metal.

	Contraction, C.	Heat, H.	Quotient, $\frac{C}{H} \times 100.$
LiCl	16.8	383	4.3
LiBr	13.0	334	3.9
LiI	5.3	257	2.1
NaCl	21.5	399	5.4
NaBr	15.0	359	4.2
NaI	8.0	289	2.8
KCl	32.2	427	7.6
KBr	26.3	398	6.6
KI	16.9	335	5.1

rine has been found by Knietzsch to be 18.6 kilojoules (*Z. elektrochemie*, **9**, 847, 1903), a number not far from that (20.5) calculated in the record of the present series of papers, and this amount is subtracted from all the commonly accepted heats of formation of chlorides. In the case of single gram atoms of chlorides only half of this quantity is subtracted.

It is worthy of note that these thermal quantities also contain the "heat of cohesion" or latent heat of liquefaction and solidification of the products. If the compounds did not condense, the heats of formation would be less. This cor-

Thus, the diminution of the quotient always accompanies a diminution in compressibility, as would be expected on the basis of the hypothesis. The nature of the case prevents a more exact mathematical treatment of these expected variations, but the unanimous verdict of this approximate treatment of them advances the agreement of fact and hypothesis to another order of approximation, in which not only the qualitative succession of magnitudes possess significance, but also the deviations from direct proportionality. Thus is afforded a strong presumption in favor of the important significance of changing atomic volume.

Many other cases of the same kind might be cited, but occasionally an apparent exception appears. For example, silver can hardly be much more compressible than zinc, and yet during the union of a mol of chlorine with the former metal a contraction of 19 milliliters occurs, while with the latter the contraction is only 13 milliliters, although the heat of formation in the latter case is almost twice as great as in the former.*

At first such an exception as this seems a serious impediment to the acceptance of the underlying hypothesis of compressible atoms, but further consideration shows at once the reason of the seeming anomaly, and, instead of being an exception, the case becomes a supporting example.

It will be apparent below that such cases are easily explained by the plausible assumption that more than one kind of internal pressure exists in a solid compound, — not only are elements probably compressed by their chemical attraction or affinity, but also the smallest particles of the resulting compound exert pressure in cohering under the influence of a cohesive attraction of less intensity.

In endeavoring to imagine the mechanism of the action of these forces, it is necessary to amplify the ordinary conception of atoms, and endeavor to imagine the behavior of each single atom under the action of the stresses to which it must be subjected. Probably each atom in such a solid as argentic chloride would be bound on one side by chemical

reaction applies so nearly equally to all that it may be neglected for the present, however.

* The molecular volume of argentic and zinc chlorides are respectively 25.8 and 46.9, and those of the metals 10.3 and 9.5, while the respective heats of formation (corrected), are 114 and 384. Since the contraction of the chlorine is probably the chief factor in the question, equivalent quantities of the two materials must be compared; therefore, in the calculation double the data of silver should be taken to correspond to one of zinc, because zinc is bivalent.

In the previous paper where this was discussed (the second of the series) a careless mistake in calculation of the silver chloride exaggerated the discrepancy.

affinity — thus forming the smallest particle or molecule of the compound — and on its other sides by a weaker affinity, causing the cohesion to the atoms belonging to other molecules — thus forming a solid mass of many molecules. Every one will grant that there are many reasons for believing that this cohesion is often much feebler than chemical affinity. For example, the former is often far more easily overcome by the introduction of heat energy than the latter. This is the case with zincic chloride, for example, a salt which boils unchanged at a temperature as low as 710° , giving a vapor which seems to possess the simplest possible formula, ZnCl_2 .

To those who are indisposed to consider seriously any hypothesis concerning the different sides of a single atom, it is only necessary to point out the benefit which has already been derived from the stereochemical hypothesis of van't Hoff and Le Bel. The present discussion carries the logic of three dimensions into another division of chemical argument.

If one side of an atom is more firmly bound than another, it is only reasonable to suppose that the more firmly bound portion is subjected to the greater pressure, and therefore compressed into the smaller volume or more flattened. It seems probable that this compressed portion must be less compressible than the portion less firmly bound, because universal experience shows that with a given substance at a given temperature, the greater the volume the greater is the compressibility. In other words, that part of an atom which is under less pressure must be more compressible than the part which is under greater pressure. Hence, a small development of energy by a change of a given small cohesive pressure for another cohesion slightly greater would correspond to a large contraction, equal to the change of volume caused by a great change in a pressure of chemical affinity already large. Thus the molecular contraction caused by the compression of cohesion may at times quite mask the atomic contraction caused by the far greater pressure of chemical affinity, because the latter is concerned with that portion of the atomic volume which has been previously compressed. There is nothing in this argument to show that the shape of the atom is *permanently* deformed or irregular, as some have supposed; it seems much more probable that in the free state every atom is spherical, and that the inequalities in the atomic surface occur only under the influence of unequal pressures, such as those which form the subject of this paper.

These considerations enable us to interpret at once the seeming anomaly concerning zincic and argentic chlorides. Zincic chloride is easily volatile, boiling, as has been said, at 710° , while argentic chloride was

found by Biltz and Victor Meyer* to be non-volatile at 1400°, and only slightly volatile at 1700°. The high boiling point of argentic chloride is one of the indications of great molecular cohesion,† and the pressure of this cohesion must produce great compression of the chlorine. Therefore we may refer the unusually great contraction taking place during the formation of argentic chloride chiefly to the physical intermolecular pressure and not so much to the essentially chemical interatomic pressure.

Even this, however, is not a complete treatment of the matter, since the metals themselves have different boiling points, and hence are probably under different internal pressures. Silver itself must be more compressed by its own cohesion than zinc is, for Nernst has shown that the former metal probably boils at a point above 1950°‡ This condition in silver must tend to counterbalance in part the effect of the great internal pressure in argentic chloride, for if silver is already more greatly compressed, it could not be so much changed as zinc by additional pressure. The much greater compressibility of chlorine is undoubtedly the reason why the great cohesion of argentic chloride diminishes the volume of a salt to a greater extent than the great cohesion of the silver diminishes its own volume.

The complication of these various conflicting tendencies is no argument against the validity of the reasoning; on the contrary, any pertinent hypothesis which does not consider them is incomplete. The volume-change occurring when two solids or liquids combine is obviously an average or composite change, depending upon the extent of both the chemical and physical compression of the factors which must be overcome, as well as upon both the chemical and physical compression of the product, — just as the heat of reaction concerns the heat absorbed in disintegrating the factors, as well as the “chemical heat” and the “latent heat” given out in the act of combining and solidifying. These considerations were neglected in comparing above the cases of haloid salts of the three alkali-metals, since these salts are very similar, and their boiling points probably not far apart.§ Moreover, the metals, too, are very similar. Hence the

* Ber. d. deutsch. ch. Ges., **22**, 727 (1889).

† Ostwald gives a table illustrating Trouton's rule (Lehrbuch, **1**, 354), which shows that with nearly related substances the boiling point is very nearly proportional to the molecular latent heat of vaporization, and that even with very different substances this is approximately true.

‡ Z. Elektrochem., **9**, 62 (1903).

§ The boiling points of these salts have not been accurately determined, but qualitative experiments of my own in tubes of fused quartz showed that all the

effect of cohesion was largely eliminated and the remaining effect could be safely ascribed to action of the pressure of chemical affinity on the different compressibilities of the elements compared in each series.

The thorough understanding of this matter is so important that it is worth while to cite other cases illustrating it. A particularly illuminating series of examples is that of the halides of zinc and cadmium. The bromides and chlorides of both these metals, as well as the metals themselves, may be easily volatilized, and their boiling points are well known; hence more is known in these cases than in almost any other concerning the relative intensities of the internal physical pressures. The work of chemical compression is again taken as equal to the heat of formation, because only a small part of the heat of formation is usually due to the heat of molecular cohesion, and the change of heat-capacity is small.

Below are given the necessary data concerning zinc and cadmium. The data are all reasonably accurate, the specific gravities being especially so, thanks to the care of Dr. Baxter and his assistants, who kindly determined three of them for use in the present paper.

From these results it is seen that in each case the contraction which takes place during the formation of the zinc halide is less than that which takes place during the formation of the cadmium salt by about five milliliters per mole, although their heats of formation are nearly equal. A part of this difference is undoubtedly to be ascribed to the cause which gives the cadmium salt a higher boiling point in each case, namely, a greater cohesive pressure in the case of the cadmic salts. A part may also be expected to be due to the fact that metallic zinc, having a higher boiling point (920°)* than cadmium (778°) — and therefore a greater molecular latent heat of evaporation or greater internal physical pressure — must be supposed to be in the more compressed state. Other indications also point to the same conclusion; for example, zinc has the smaller coefficient of expansion, the smaller molecular volume, the greater hardness, and the larger “energy quotient,” (a quantity having the dimensions of pressure which is obtained by dividing the atomic heat by the atomic dilation).† Since each of these latter qualities is not a function

chlorides boil considerably over 1200° , and not far apart. Lithic chloride seemed to be slightly the more volatile of the three. The melting points are all near together, — of the bromides and iodides as well as of the chlorides, — and in similar salts of this kind it is not very dangerous to infer similar boiling points from their known melting points.

* Zeitschr. phys. Chem., **42**, 118 (1902); Compt. Rend., **131**, 380 (1900).

† These Proceedings, **37**, 1 (1901).

Salt.	Boiling Point.	Specific Gravity.	Molecular Volume.	Sum of Atomic Volumes.	Contraction.	Heat of Format'n. (kj.)
ZnCl ₂	730 *	2.91 ‡	46.9	9.5 + 50 = 59.5	12.6	388
CdCl ₂	910 †	4.05 §	45.4	13.0 + 50 = 63.0	17.6	371
Difference					5.0	
ZnBr ₂	650 *	4.22	53.4	9.5 + 51 = 60.5	7.1	318
CdBr ₂	810 †	5.20 §	52.2	13.0 + 51 = 64.0	11.8	315
Difference					4.7	

of the average internal pressure alone, but also of other variables, none of them alone furnishes certain evidence; but when all point in the same direction the probability of their combined verdict is great. If then, zinc is in a more compressed condition than cadmium, it should not contract so much as cadmium upon further compression. Here the difference in cohesion of the two metals affects the result in the same direction as that of the salts, instead of in the opposite direction, as in the case of silver and zinc.

These two probable circumstances — namely, the greater internal compression of the salts of cadmium and the less internal compression of metallic cadmium — seem to me quite enough to afford an explanation of the fact that greater contraction occurs during the formation of cadmic salts than during the formation of zincic salts.

On comparing the chlorides with the bromides the result is essentially similar. The contraction on forming bromides is less in proportion to the energy-change than that on forming chlorides, chiefly because bromine is less compressible than chlorine, but partly also because the resulting bromides are less compressed than the chlorides, judging by their lower boiling points.

* Freyer and V. Meyer, Ber. d. deutsch. ch. Ges., **25**, 622 (1892).

† Carnelley and Carleton-Williams, J. Chem. Soc., **37**, 125 (1880).

‡ Baxter and Lamb, Am. Chem. Journ., **31**, 229 (1904).

§ Baxter and Hines, Am. Chem. Journ., **31**, 220 (1904). The previous data, obtained by Knight under the direction of F. W. Clarke, were much too low. Sill. J., (3) **16**, 202 (1878); Am. Chem. J., **5**, 240 (1883).

|| Richards and Rogers, Z. anorg. Chem., **10**, 6 (1895).

Thus, all the variations in the zinc and cadmium series seem to be not only explicable but necessary.

In order to make the statement of possible types more complete, it is worth while to cite the circumstances attending the formation of an easily volatile endothermic compound from two elements less volatile. Here we should expect the compound to occupy much *more* space than the elements, since both the chemical and physical internal-pressures are less after combination than before. Such a case is that of carbon disulphide, whose formation involves the absorption of 93 kilojoules of heat, accompanied by an *increase* of volume of 25 milliliters (from 35 to 60 milliliters) per gram molecule. This very large increase of volume is too great to be referred to the decrease in either the chemical or the physical pressure alone; its magnitude, therefore, shows that both these causes are working together to cause a change of volume, as the hypothesis predicts. It must be borne in mind that a given output of energy in the change of physical compression caused by cohesion would have a more marked effect on the volume than the same output in the change of chemical affinity, because the cohesive attraction acts on the expanded and easily compressible part of each atom — namely, the outside surface of the molecule, which is compressed *only* by comparatively slight pressure of its cohesion with other molecules. In short, when the existing pressure is small, the change of volume for a given additional change of pressure will be large, with a given expenditure of energy.

That exothermic non-volatile sulphides behave in the usual way, and hence that this behavior of carbon disulphide does not depend upon any peculiarity of sulphur, is seen by comparing the contraction of 55 milliliters which occurs during the formation of potassic sulphide with that of 2 milliliters in the case of argentic sulphide, the respective heats of formation being 423 and 14.

It is easy to show that these principles generalize and correct a great part of the irregularities in the curve giving the relation between heats of reaction and decrease in volume. The majority of the other irregularities which still remain are undoubtedly due to inaccurate data. The published values of specific gravities are notoriously untrustworthy, often because they have been based on salts only partially dehydrated. For examples, the specific gravities of zincic and cadmic bromides are usually supposed to have the values 3.64 and 3.79, instead of the true values 4.22 and 5.20 respectively, — an error of over twenty-five per cent in the latter case. Again, heats of formation are often untrustworthy. For example, the value for carbon tetrachloride is given by Thomsen as

76 kilojoules, and by Berthelot and Mantignon as 226 kilojoules.* In such cases one is at a loss as to the true value, without new experimental data, and is unable to apply intelligently the principles under consideration.

It is not to be expected, however, that even when all the data have been correctly determined the agreement should be mathematically precise, especially when solids are concerned, on account of the complexity of the problem, and the fact that a given substance often assumes different solid forms. In nearly all cases, it is true, the relation of the different solid phases of a given substance accords qualitatively with the principles above: — the formation of the more compact phase evolves heat, and hence this phase gives a less heat of reaction with other substances,† indicating a state of greater compression. This is true, for example, in the case of sulphur, phosphorus, and carbon. In such cases, the output of heat of allotropic modification has the same sign as the contraction in volume, and these quantities add respectively to the heat evolved, and to the change of volume during any reaction, not affecting the qualitative relation.

In some cases, however, the act of polymerization or of solidification seems to involve an anomalous expansion of volume, an apparent inconsistency which needs further discussion. There can be no doubt that the explanation given in a previous paper‡ affords the most probable interpretation of this fact. The explanation runs as follows, — it will be amplified below: —

“In those cases where there is a transition from a more compressible union to a stabler, less compressible one, involving more work of compression, solidification would involve increase of volume, as in the case of water.”

This possibility might be discussed as an abstraction; but it becomes much clearer when a specific case is considered. Of course, such a consideration presupposes a knowledge of the nature of the molecular change which takes place in the substances, and but little is known concerning such changes. Hence, the evidence must in most cases be vague and rather unsatisfactory. It seems to me, however, that enough is known concerning at least a single case, that of the solidification of water, to allow its interpretation to serve as a type; and if the discussion is viewed as a possible concrete example of a general principle,

* See Ostwald, *Lehrbuch*, **2** (1), 175 (1893).

† Petersen, *Zeitschrift für physikalische Chemie*, **8**, 611 (1891).

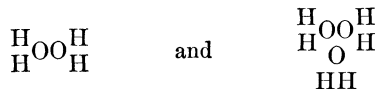
‡ Richards, *These Proceedings*, **37**, 407 (1902).

rather than as a definite statement of fact, this risk of partial mistake in some of the details can do no serious harm.

In the first place, there are many well-known reasons for believing that liquid water is partly polymerized, and that its polymeric form is more bulky than its simple form. The admirable experimental work of Ramsay and Shields on surface tension* and the interesting logic of van Laar† may be cited as among the work affording a strong presumption of this partial "association." The determination of even the average extent of the polymerization is a more difficult matter, as may easily be seen by studying the papers of van der Waals‡ and Ramsay§ upon the subject. A conservative estimate is perhaps that given by Ramsay in his last mentioned paper — namely, the estimate that water at 0° has an average molecular weight of 1.7×18 , and at 140° an average molecular weight of 1.3×18 . Thus the liquid under ordinary conditions seems to consist of a mixture of $(\text{H}_2\text{O})_n$ and H_2O , the latter preponderating at high temperatures.|| Presumably ice consists wholly of $(\text{H}_2\text{O})_n$.

The determination of the magnitude of n in the above polymer is even more difficult than the determination of the exact average extent of polymerization; but fortunately for the present discussion neither of these points is crucial as far as it is concerned. Usually n is taken as 2; but there seem to me several reasons for believing it to be 3, an assumption which would correspond to other familiar polymers and with the well-known trigonal symmetry of ice.¶ In this case, of course, less of the polymeric form would be needed to account for the anomalous properties of water, than if its polymerized formula were $(\text{H}_2\text{O})_2$.

In any event, because of the well-marked univalence of hydrogen, every one will concede that the polymer is probably formed by the union of oxygen to oxygen. The two most probable structural forms will then be



Either assumption will satisfy the requirements of the present argument.

* Ramsay and Shields, *Zeitschr. phys. Chem.*, **12**, 433 (1893).

† Van Laar, *ibid.*, **31**, 1 (1899).

‡ Van der Waals, *Zeitschr. phys. Chem.*, **13**, 714 (1894).

§ Ramsay, *Zeitschr. phys. Chem.*, **15**, 106 (1894).

|| This conclusion does not exactly agree with the highly hypothetical assumptions of Sutherland. *Phil. Mag.*, (5) **50**, 460 (1900).

¶ The crystal form of ice is cited by Sutherland as a reason for assuming $(\text{H}_2\text{O})_3$.

Having thus decided that the existence of a polymeric form is probable, the next step is a study of the probable mechanism of the act of polymerization. In a simple molecule of water, for reasons given above, it is usually assumed that each hydrogen atom is attached to the oxygen, HOH. When a molecule thus constituted coheres with other molecules to form a liquid, there are two typical situations attainable by the atoms of neighboring molecules. The atoms of each kind may be in juxtaposition with the same kind of atoms, or hydrogen of one molecule may be in the neighborhood of oxygen of another. If neither of these two situations involved a great excess of cohesive attraction over the other (the normal condition of an unassociated liquid), both situations would be present to about equal extents. From what has been said before, this may be supposed to be the case in liquid water at high temperatures.

What now happens when the water is cooled? Since there is every reason to believe that the act of polymerization evolves considerable heat, this act will tend more and more to occur as the temperature becomes lower, according to the theorem of Le Chatelier. All our experimental evidence points in this direction. But this increasing polymerization will involve an increasing shift of the cohesive attraction from the condition of equal distribution to that in which oxygen is in juxtaposition with oxygen, and hydrogen with hydrogen.

The effect of such a shift as this upon the volume will depend entirely upon the relative compressibilities of the elements concerned, under the peculiar circumstances to which they are exposed. There is good reason to believe that under conditions as parallel as possible, oxygen is less compressible than hydrogen. For example, pentane (C_5H_{12} , boiling at 38°), containing much hydrogen, is half again as compressible as sulphur dioxide (SO_2 , boiling at -10°) if the figures are compared at corresponding temperatures (0° and 50° respectively, each a corresponding number of degrees above the boiling point).^{*} Since sulphur in combination is probably at least as compressible as carbon, the difference here is to be referred primarily to that between hydrogen and oxygen. The study of many other, indeed all the known, compressibilities of compounds rich in hydrogen, leads to the conclusion that the compressibility of hydrogen is great, and that of oxygen smaller. This is not indeed surprising, since the average density of the oxygen in combination is about eight times as great as that of hydrogen, if Kopp's atomic

^{*} Landolt and Börnstein Tabellen, p. 268 (1894). The values were found by Grimaldi and by Colladon and Sturm.

volumes be taken as an approximate criterion, and density seems to be an important factor in determining compressibility.*

Assuming, then, that oxygen is less compressible than hydrogen, and that the act of polymerization would involve the severing of cohesive attraction of oxygen to hydrogen, and the substitution of the attraction of oxygen for oxygen, the hydrogen, on being freed and but little attracted by its neighboring hydrogen, would expand more than the oxygen could contract. Thus an increase of volume would result, even although the energy developed by the oxygen in combining with itself might be considerable. Here, as before, it must be borne in mind that a given change of volume in a compressible substance corresponds to a smaller amount of work than the same change of the same volume of a slightly compressible substance.

In the act of solidification the oxygen-hydrogen cohesion would all be severed, and the system would suffer a sudden expansion in consequence. Thus may be explained the irregular coefficient of expansion of water, and the abnormal expansion on solidification; as before, the apparent exception really supports the argument.

Another although essentially similar case is the somewhat unusual one in which an *elementary* substance on cooling assumes the form of a phase of less density. The most striking case of this anomaly is that of tin, which possesses at least two different forms with specific gravities of 7.3, and 5.8 respectively, the more dense being stable at high temperatures, and the lighter at low temperatures.† Even such a case as this is not inexplicable, however; for if the denser form consists of atoms compressed nearly equally on all sides, an expansion accompanied by evolution of heat might occur through a polymerization involving a greater compression on one side of each atom, with the partial release and consequent expansion of the other side. Because the compressibility diminishes with decreasing volume, the expansion on the sides of the atom partially released might easily exceed the contraction on the compressed side of the atom. If this is really the case with tin, one would expect the irregularly constituted gray tin to possess a smaller tenacity

* According to Dupre's rule, compressibility is inversely as the square of the density. This relation only holds strictly true with analogous compounds, but nevertheless serves as an index of the importance of density.

† See Cohen, *Zeitschr. phys. Chem.*, **30**, 601 (1899), etc.

The other possible varieties of tin may be explained by arguments similar to these. See Rammelsberg, *Jahresbericht*, 1870, pp. 358, 724; Shepherd, *J. Phys. Chem.*, **6**, 519 (1902).

than the evenly compressed white tin, because tenacity must depend upon the weakest cohesive attraction existing in a substance, just as the strength of a chain is the strength of its weakest link. As a matter of fact, gray tin seems to possess far less tenacity than white tin, for the former is always described as crumbling to powder; hence the fact is consistent with this interpretation. The situation is far too complicated, involving the simultaneous action of too many intensities of pressure to attempt at present a precise mathematical solution, or to afford a basis for the discovery of the reason why tin in particular acts in this peculiar way. The explanation above is given only to show that this kind of case, instead of offering insuperable objection to the theory of compressible atoms, accords with it and affords a means of predicting an entirely different property of the anomalous form — namely, its slight tenacity.

Besides the changes of volume which may thus be effected by the polymerization of a solid or liquid, changes of volume are undoubtedly occasioned by the exigencies of crystal form. These will be considered in a subsequent paper. Taking into account all these possible irregularities, it is not at all surprising that the changes of volume do not exactly correspond to the heats of formation in chemical reactions; indeed, it would be incredible that the correspondence should be exact. Nevertheless, in spite of these expected and reasonable irregularities, enough obvious regularity still persists to show the general tendency, and to make highly probable the fundamental statement that the atomic volume is not a constant, but is a function of the total pressure (internal and external) and the temperature.

It has been suggested above that in general the lower the boiling point, the greater should be the compressibility, — because a low boiling point indicates slight molecular cohesion; and when the pressure upon the surface of the molecules is small, these molecules should be in an expanded condition, and therefore easily compressible. This postulate is supported not only by the facts given above, but also by many other data of the same kind. Of course the relation is sometimes partly hidden by the specific nature of the elements concerned; hence it is shown most clearly by the comparison of isomeric organic substances. In any complex molecule of this kind, it is true that the compressibility must be an average value; for the application of an outside mechanical pressure must add not only to the pressure of cohesion between the molecules, but also to the various affinity-pressures which exist between the atoms. Nevertheless, the change of volume produced by the former of these effects

should be so much greater than that produced by the latter (because the affinity-pressure must be already so great) that usually the former alone would be expected to become manifest by its effect. Data illustrating these inferences are given below.

Another property, going hand in hand with this relation of compressibility and boiling point, is density. It is to be expected that of two similar substances, that with the higher boiling point and the less compressibility, being subject to greater internal pressure, should be the more dense.

A few figures, representing several classes of compounds, are given below to show that in general these considerations are supported by fact.

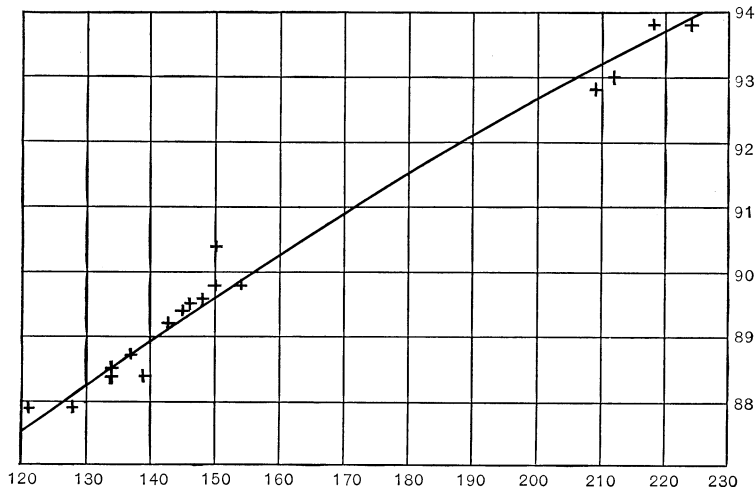
RELATION BETWEEN BOILING POINTS, DENSITIES, AND COMPRESSIBILITIES OF ISOMERIC COMPOUNDS.

Substance.	Boiling Points.	Density at 0°.	Compressibility $\times 10^6$.
Ethyl butyrate	120°	0.899	93
Methyl valerate	127°	0.909	91
Isopropyl alcohol	83°	0.788	103
Propyl alcohol	97°	0.804	97
Isopropyl chloride	37°	0.874	
Propyl chloride	46°	0.916	
Paraxylol	138°	0.880	
Orthoxylol	148°	0.893	

In each of these cases, the higher boiling point accompanies greater density and less compressibility. The last-named property has been determined in so few cases that the material for generalization is small; but as far as they go the data all point in the same direction.* On the other hand, so many densities have been determined that the usual parallelism of this property with the boiling point is easily verified. Among

* Gartenmeister Liebig's Annalen, **233**, 309 (1886), found that esters with highest boiling point have the least coefficient of expansion — a property that very usually varies in the same direction as compressibility.

many interesting groups of compounds, that having the common formula $C_7H_{14}O_2$ is especially complete and comprehensive, the boiling points ranging from 224° with normal heptylic acid to 121° with isopropyl isobutyrate, while the densities range from 0.938* to 0.879. Among the seventeen compounds in this group whose data are to be found in Beilstein's invaluable handbook, the density of only one (methyl caproate) deviates more than 0.005 from its place in the parallel series, the density steadily diminishing as the boiling point diminishes. This is shown in the following diagram, where centigrade boiling points are recorded as abscissae, and densities at 0° as ordinates. Clearly the correspondence of density to boiling point is too close to be the result of accident.

BOILING POINTS AND DENSITIES OF SUBSTANCES $C_7H_{14}O_2$.

The divergent point on the ordinate 150° represents methyl caproate, and that less divergent on the ordinate 139° , isoamyl acetate.

The other substances, named in order, are isopropyl isobutyrate, isopropyl butyrate, propyl isobutyrate, ethyl isovalerate, butyl propionate, propyl butyrate, ethyl valerate, isobutyl propionate, amyl acetate, methyl isobutyl acetate, hexyl formiate, isomylacetic acid, isoheptylic acid, iso-onanthic acid, and heptylic acid.

This regularity is so obvious that it must have been noticed before; but nevertheless, the plausible hypothetical explanation of it, depending

* This value is Franchimont's (Ann. Chem. Phys., **165**, 242 (1873) corrected to 0° with the help of Zander's value for the coefficient of expansion. Ibid., **224**, 70 (1884). Franchimont's value is chosen because his substance was the purest, having a melting point of -8° .

upon the theory of compressible atoms, has probably not before been emphasized.

From these examples it is clear why the density must usually be taken at about the boiling point in order to obtain additive values for the molecular volumes of organic substances, as Kopp found. Those substances which possess a high boiling point, or by inference great pressure of cohesion, would be expected to be in a highly compressed state. When compared at the same temperature, the molecular volumes of the more compressed material will therefore be smaller than the molecular volumes of the less compressed material; but by heating the more compressed material it may be expanded until the thermal expansion at a definite point replaces the volume lost by this cohesive compression. The higher the boiling point, the greater must be the cohesive compression, and the higher will be the rise of temperature needed to counteract it. This corresponds exactly with the fact. In many cases (those of fat acids, esters, and ethers) it happens that the required rise of temperature not only varies in the same direction as the boiling points, but also closely corresponds in magnitude with their difference. In others, especially the alcohols, aldehydes, halides, and aromatic compounds, the deviations are considerable. In the case of butyl alcohol, for example, the liquid must be heated under pressure to a point about 35° above its boiling point in order that it may attain the volume required by Kopp's rule, being five per cent too small in volume* at its boiling point.

Deviations of this kind seem to indicate clearly that although in general a substance possessing a higher boiling point must be heated to a higher temperature in order that the molecular volume may become a precisely additive quantity, the exact temperature needed is determined by the concerted action of too many variables to be precisely determined. The fact that in a minority of cases the boiling point itself is a suitable point of comparison seems to be accidental.

The existence of irregularities in the above described relation of density to boiling point might have been predicted by the logical application of the idea of compressible atoms; for evidently *chemical affinity* causing atomic rearrangement within the molecule might cause a change of atomic compression, and hence of density, without greatly affecting the *cohesive* attraction, thus leaving the boiling point unchanged. Accordingly, the usual relation between boiling point and density might be marred in some cases.

* See Ostwald's Lehrbuch, 1, 369 (1891).

In seeking for quantitative verification of such an effect, the irregularities themselves are the best guide to their cause, hence the alcohols, already quoted as abnormal in their behavior, serve as useful examples. Fortunately, too, the heats of formation of enough alcohols are known, in order to provide a clue as to a change of the internal stress within the molecule. Below is given a brief table typically illustrating the point.

THE EFFECT OF INTERNAL ATOMIC REARRANGEMENT ON DENSITY.

Alcohols.	Boiling Point.	Specific Gravity at 20°.	Heat of Combustion of Liquid.* (Ostwald Calories.)	Latent Heat of Evaporation calculated by Trouton's Rule. (Ostwald Calories.)	Heat of Combustion of Vapor. (Ostwald Calories.)	Heat of Formation of Vapor from the Elements. (Kilojoules.)
Propyl	97°.4	0.804	4803	96	4899	312
Isopropyl	82°.8	0.789	4783	92	4875	322
Isoamyl Dimethyl ethyl carbinol }	131°	0.825	7939	105	8044	376
	102°	0.825	7885	97	7982	402

In the case of the propyl alcohols given in this table, the usual relation exists, — the density is greater where the boiling point is greater, — but in the case of the amyl alcohols, on the other hand, an anomaly appears. In the latter case the densities of the two compounds given in the table are identical, although their boiling points are 29° apart.

The most plausible explanation of this circumstance lies in the assumption of increased internal atomic compression, due to the peculiar structure of dimethyl ethyl carbinol; a compression which has nothing directly to do with the cohesive attraction and the boiling point, because these are concerned only with the superficial attraction of the molecules. By causing decrease in volume this internal stress serves to conceal the increase in volume due to a lesser pressure of cohesion in the lower-boiling liquid. This hypothetical inference is supported by the heats

* These figures are due to Louguinine (Am. chim. phys., (5) **21**, 139 (1880)). Thomsen's figures show similar differences, although in a more exaggerated degree. Qualitatively they would lead to the same conclusion.

of formation of these compounds. Dimethyl ethyl carbinol has a distinctly greater heat of formation than isoamyl alcohol, while in the case of the propyl alcohols there is no great difference between the heats of formation of the isomers. Since a greater heat of formation usually signifies greater affinity, since greater affinity must cause greater pressure, and since greater pressure must diminish the volume, it appears highly probable that in the case of the amyl alcohols a greater stress within the molecule in one case may cause an increase in the density which is enough to compensate for the decrease of density on the molecular surface due to a smaller pressure of cohesion between different molecules. Thus, the apparently anomalous behavior of the alcohols not only offers no argument against the principles involved, but rather supports the other arguments in favor of those principles.

These cases may be taken as typical; and probably most of the variations in density, compressibility, and boiling point may be explained in this way. As before, however, it is not to be expected that every case could exactly correspond, for the densities, compressibilities, and heats of formation of complex compounds of this kind represent average values, and much would depend upon the constitution of the body, and the arrangement of the atoms in space. As in the case of water and tin, cited above, it might easily happen that a considerable excess of heat of formation in a given case might be evolved by a shift from a more compressible union to a less compressible one, involving the expenditure of more chemical energy without causing a decrease in volume.

It is evident upon consideration that all these typical cases are really dependent for their interpretation upon the following very simple conceptions: first, that internal pressure, due to both cohesive attraction and chemical affinity, must tend to diminish the volume of condensed systems (*i. e.* solids and liquids); secondly, that the greater the pressure, the greater is this tendency; and thirdly, that, other conditions being equal, a substance already much compressed by internal pressure suffers less contraction upon subjection to additional pressure than one but little compressed. The circumstance that the facts above cited are all consistent with this obvious logic affords a strong presumption that it is correctly applied.

The existence of these different intensities of internal pressure affords a basis also for explaining the partial parallelism and frequent apparent irregularity of the various physical properties of material, such as tenacity, hardness, ductility, malleability, etc., and the relation of these properties to boiling points. For example, in order that a liquid may vaporize

monatomically as zinc does, even the strongest tie binding each atom must be broken; on the other hand the *tenacity* of the metal could be no greater than the cohesion of the weakest tie, as has already been pointed out, in the case of tin. If all the atomic ties were nearly equal in each of two cases, that is, if the atoms were equally compressed on all sides, tenacity and boiling point would be expected to vary in a parallel manner. In a similar way the other physical properties might be discussed in relation to the varying intensities of cohesive and chemical attraction; but the complete discussion involves more knowledge concerning the extent and nature of polymerization in solids than is at present available; hence it must be postponed.

In conclusion, it may be noted that the hypothesis of compressible atoms is consistent with either of the two alternative hypotheses concerning the ultimate nature of material — namely, the corpuscular conception so popular to-day, and the hypothesis assuming the atom to be an ultimate continuous although compressible aggregation.

Moreover, it is not a necessary consequence of the facts discussed above that the atom should have a very sharply defined surface, — the concentration of its substance may increase gradually as the centre is approached. On the other hand the fact that a definite volume is attained, and that the compressibility decreases greatly with diminishing volume, seems to prove that the distending effect increases much faster than the law of inverse squares governing the usual forms of attraction. The discussion of these questions is best deferred until some of the more immediate consequences of the hypothesis have been studied.

SUMMARY.

In this paper the following conclusions, based upon new data of known accuracy, are attained: —

(1) Among compounds of lithium, sodium, potassium, chlorine, bromine, and iodine, it is shown that in every case the compound of a more compressible element is formed with a greater decrease of volume than the compound of a less compressible element, other conditions being equal.

(2) From a study of data concerning the chlorides of silver, the chlorides and bromides of zinc and cadmium, and carbon bisulphide, it is shown that the more volatile the substance (i. e. the slighter its cohesive attraction), the greater is the molecular volume, other conditions being equal.

(3) It is pointed out that a given change in chemical energy produces a smaller change of volume than the same change of cohesive energy produces.

(4) These typical facts are explained by the assumption that both chemical affinity and cohesive attraction exert a compressing effect upon solid or liquid substance, and that the chemically tied part of each atom is more compressed than that which is subject only to cohesive pressure.

(5) Polymerization and crystallization are shown to be capable of causing irregularities. The cases of water and tin are discussed in detail as types, and it is shown that there is nothing in these cases contradictory to the explanation given above.

(6) From the comparison of many isomeric organic compounds, it is shown that the explanation covers also their relations of densities, compressibilities, and boiling points, including even some of the apparent irregularities in those relations. Thus is shown the reason why additive molecular volumes are obtained only when, of two liquids, the less volatile (i. e. the more cohesive) is heated to a higher temperature.

(7) It is suggested that these varying intensities of internal pressure are adequate to explain the variety of other physical properties, such as tenacity and malleability.

(8) These considerations, by accounting numerically in detail for most of the irregularities in the more obvious facts discussed in previous papers, afford increased evidence as to the significance of changing atomic volume, and increased support for the theory of compressible atoms.

CAMBRIDGE, MASS.

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